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Symmetry-driven phase transformations in single-wall carbon-nanotube bundles under hydrostatic pressure

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Ab initio calculations on (10,10) and (12,12) single-wall carbon-nanotube bundles show that the nature of the phase transformation under hydrostatic pressure is determined by the symmetry of the nanotubes. Bundles of (10,10) nanotubes that are incommensurate with the hexagonal lattice, have small deviations from hexagonal symmetry of the lattice even at zero pressure. A transition to monoclinic structure is obtained at about 1 GPa within the generalized gradient approximation such that the nanotubes transform to an oval shape. However, in the local-density approximation the monoclinic phase is retained even at zero pressure once the transformation has occurred. Bundles of (12,12) nanotubes are commensurate with the hexagonal symmetry of the lattice and show no transition even up to 6 GPa pressure except for a polygonization of the initially cylindrical nanotubes into a hexagonal shape. These results would resolve the contradictory conclusions obtained from experiments.

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Understanding of the mechanical behavior of single-wall carbon-nanotube bundles (SWCNTB's) is important for their potential usage in devices, hydrogen storage media,[1] light weight batteries,[2] and high strength composites. There are indications[3–6] that a structural transformation occurs in SWCNTB's under hydrostatic pressure. However, the nature of this transition is not clearly understood. There is evidence that polygonization of the nanotubes occurs under pressure,[4] whereas in some model calculations[5] a change in the structure of the nanotubes as well as the underlying lattice has been obtained. These could affect the electronic properties of the bundles and hence their applications. Here we report *ab initio* studies on (10,10) and (12,12) SWCNTB's under pressure that show the transition to be dependent on the symmetry of the nanotubes.

Experimental high-pressure studies on SWCNTB's have provided conflicting results. Disappearance of the radial breathing modes between 150 and 200 cm^{-1} in Raman spectra[3] at around 1.5 GPa was interpreted to be due to *polygonization*, a hexagonal distortion, of the initially cylindrical nanotubes. Tang *et al.*[4] reported a similar observation from synchrotron x-ray diffraction in the same pressure range and an irreversible transformation beyond 5 GPa. The nanotubes were reported to deform to a hexagonal shape. Peters *et al.*[5] have reported a reversible structural transformation at ≈ 1.7 GPa from Raman spectroscopy. Their universal force field simulations on (10,10) SWCNTB's showed a structural phase transition from a near-hexagonal to a monoclinic phase accompanied by a change in the nanotube cross section from circular to an oval shape. In the following, we refer to this as *ovalization* of the nanotubes. A large and reversible compression of SWCNTB's under high pressure was also reported[6] using a piston-cylinder apparatus. It was interpreted to be due to crushing and flattening of the ropes of nanotubes. However, ovalization could not be confirmed. Polygonization of nanotubes of diameter larger than 25 Å was predicted[7] in bundles even at zero pressure from model calculations such that the nanotubes flatten against each other under the van der Waals attraction, forming a honeycomb structure. Evidence of polygonization of nanotubes of 17 Å diameter has been recently obtained[8] from high-resolution electron microscopy and simulations with a *constraint of hexagonal lattice*. More recently, Raman spectroscopy studies[9] on SWCNTB's up to 9 GPa show the frequency of the radial modes to upshift and the intensity to decrease with an increase in pressure. While this is a general result of all Raman spectroscopic studies, the value of the shift and the positions of the peaks differ. It is surmised that this could be due to the presence of nanotubes of different diameters[10] in bundles. Also, even in samples with nanotubes of nearly the same diameter, differing chiralities could affect the properties of SWCNTB's. This is evident from the fact that in one sample, a discontinuous change has been obtained[9] in the radial mode intensity at 2 GPa while in another sample, the radial modes could be observed even up to 7 GPa. The latter result was considered an indication that the ovalization found by Peters *et al.*[5] does not occur in actual SWCNTB's. *Ab initio* studies could provide useful insight in understanding the experimental results as well as the changes in the electronic structure upon deformation. We consider here *crystals* with a single armchair type (10,10) or (12,12) nanotube per unit cell[11] in order to study the effects of symmetry of nanotubes on pressure behavior. These have diameters close to the observed values in experiments[12] and are, respectively, incommensurate and commensurate with the hexagonal lattice.

The calculations have been performed using an *ab initio* ultrasoft pseudopotential, plane-wave method.[13] The cutoff energy for the plane waves is 360 eV. The exchange-correlation energy is calculated within both the local-density approximation (LDA) and generalized gradient approximation (GGA).[14] Reciprocal space integrations are performed with the Monkhorst-Pack special **k**-points method[15] using up to 29 **k** points along the reciprocal of the nanotube axis.[16] Band-structure calculations perpendicular to the reciprocal of the nanotube axis show the dispersion near the Fermi level to be less than 0.5 eV. The structural energy differences are found to be quite small ($\approx$meV). Therefore, the convergence

criterion for the structural optimization is taken such that the force on each ion is <5 meV/Å. At low pressures the interaction between the nanotubes is mainly van der Waals type but weaker than between graphene layers due to reduced overlap. It generally leads to a hexagonal array of nanotubes in bundles. Test calculations on intergraphene interactions using LDA gave a value of 0.3353 nm for the intergraphene distance, in excellent agreement with the experimental value of 0.3355 nm. However, the GGA value of the intergraphene distance is too high (0.460 nm). Therefore, the LDA results are far superior as compared to GGA. However, at very high pressures the overlap contribution to bonding may become more pronounced and the GGA could provide a better representation. Therefore, GGA (LDA) could effectively give the lower (upper) bounds for the intertube bonding. In the following, the unbracketed (bracketed) results refer to GGA (LDA), unless otherwise stated.

Calculations with the constraint of hexagonal lattice show deformation under hydrostatic pressure such that the cross section of the nanotubes gradually changes from circular to hexagonal without any abrupt transformation. This is in agreement with the results of Lopez *et al.*[8] However, detailed calculations without any constraint show a slight difference in the lattice vectors **a** and **b** even at zero pressure that make the (10,10) nanotube bundles monoclinic. Moreover, the nanotubes are not exactly cylindrical but slightly oval (the ratio of the long and short tube radii being close to 1.02 in both the GGA and LDA) in the distorted hexagonal lattice. The lattice constants *a* and *b* are 16.54 and 16.51 Å, respectively, and the intertubular distance (*d*) is ≈ 3.12 Å in LDA. These agree with the results of Tang *et al.*[4] of about 16.5 and 3.12 Å. The value of *d* is lower than in the case of graphite due to the curvature of the graphene sheets. The GGA values of *a* and *b* (≈ 17.5 Å) are significantly higher. In the following, we discuss only the results obtained without any constraint on the lattice symmetry.

Under hydrostatic pressure the (10,10) SWCNTB's initially remain in the near-hexagonal phase. The nanotubes mostly retain their cylindrical shapes while the main effect is a reduction in the intertube separation and an increase in the difference between the values of *a* and *b* lattice parameters. At 2.5 (1.2) GPa, a sudden transformation of the nanotubes occurs to an oval shape [Figs. 1(a) and 1(b)] accompanied by a transformation of the lattice from the near-hexagonal to a pronounced monoclinic structure (Fig. 2). The interatomic distances within a tube and the lattice vector along the nanotube axis remain nearly the same in the whole pressure range. In order to locate the transition pressure, further calculations are done by decreasing pressure in steps of 0.2 GPa or less. Figures 2(a) and 2(b) show the variation of the lattice parameters perpendicular to the nanotube axis as a function of pressure during loading and unloading obtained with LDA and GGA. It is seen that the monoclinic structure is retained up to 0.4 (0.0) GPa. A comparison of the enthalpies of the near-hexagonal and the monoclinic phases shows that the transition occurs at about 0.9 (-0.16) GPa (Fig. 3). The GGA transition pressure is in reasonable agreement with the experimental findings of a structural transition at 1.5 to 2.0 GPa.[3–5,9] However, different chiralities and diameters in actual SWCNTB's may affect this comparison. Nanotubes of about 1.34 nm diameter, such as (10,10), have no chirality commensurate with threefold symmetry and therefore, their bundles will undergo ovalization under pressure. However, larger diameter nanotubes have chiralities commensurate with threefold symmetry that, as we shall show, have no tendency for ovalization under pressure and their presence in a bundle could impede the structural transformation. Also, experiments have been reported under conditions of increasing pressure only, so that the experimental transition pressure could be considered as an upper bound.

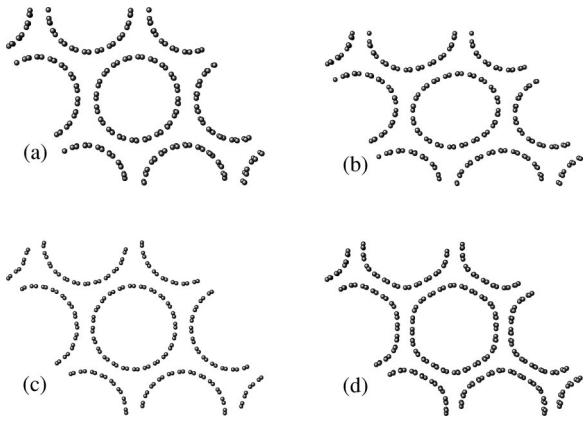

FIG. 1. (a) Near-hexagonal structure of (10,10) SWCNTB's at zero pressure with nearly circular nanotubes, (b) oval (10,10) nanotubes at 2 GPa in the monoclinic structure, (c) and (d) show the hexagonal structure of (12,12) bundles at zero (cylindrical nanotubes) and 6 GPa (polygonization), respectively.

Figure 2 shows hysteresis in the lattice constants. Their discontinuous change makes the transition in (10,10) SWCNTB's first order. The latent heat of transformation is about 0.7 (0.2) meV/atom. This is to be compared with an internanotube binding energy (BE) of 1.2 (10.6) meV/atom. This is computed by moving the nanotubes 0.5 nm farther apart than in the near-hexagonal structure at zero pressure followed by a structural relaxation of the nanotubes in frozen unit cells. The LDA value of the BE is comparable to 5 meV/atom obtained by Lopez *et al.*[8] using a model potential and about 15 meV/atom by Tersoff and Ruoff[7] based on van der Waals interactions. It is surprising that in the GGA, the latent heat of transformation is such a large fraction of the intertubular BE, while in LDA the latent heat is very small. The latent heat of transformation is given by the transition pressure times the volume difference in the two phases. The LDA latent heat is small as the transition occurs near zero pressure. The volume difference between the near-hexagonal and monoclinic phases at the transition pressure is of the order of 1%. The volume difference increases with pressure, but the shape of the nanotubes changes more significantly. At the transition pressure the *a* and *b* lattice parameters of the monoclinic phase differ by 9% (6%). The long and short radii of the oval-shaped nanotubes differ by about the same amount. This suggests that it might be possible to use SWCNTB's as nanoscale actuators, if a suitable method for driving the transformation can be found. Alternately, the pressure-induced change in the nanotube cross section could

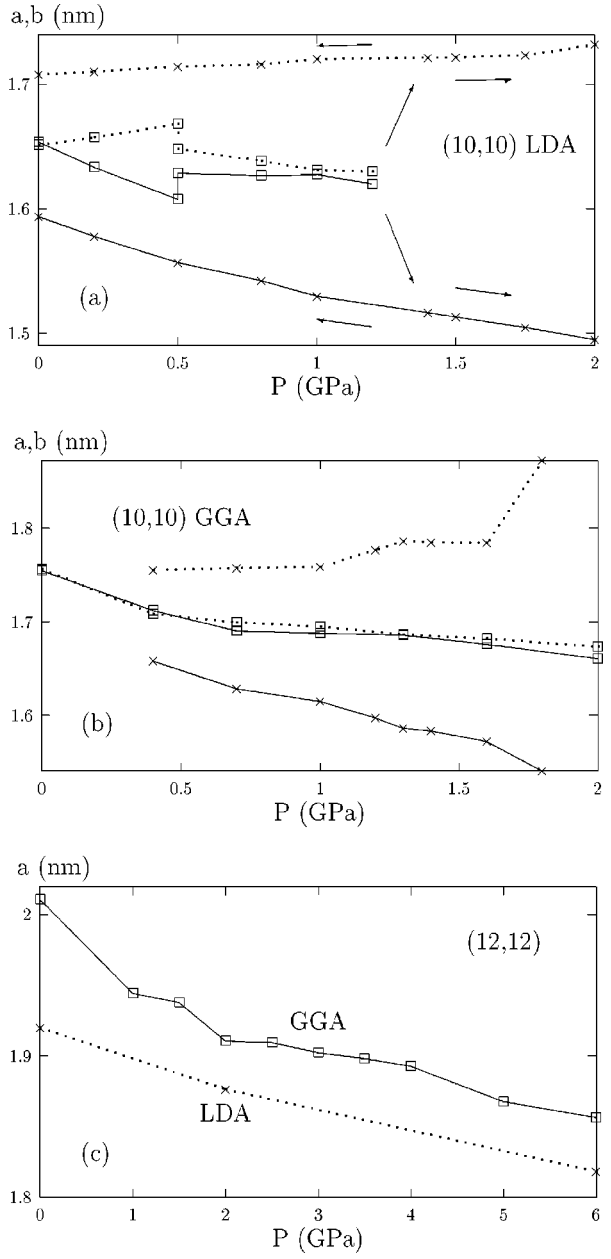

FIG. 2. Lattice parameters perpendicular to the SWCNT's as a function of hydrostatic pressure. (a) and (b) show LDA and GGA results for (10,10) bundles, respectively, while (c) corresponds to (12,12). For (10,10), squares (crosses) correspond to near-hexagonal (monoclinic) structure. In GGA, the phase transformation occurs in (10,10) bundles upon increasing the pressure from 2.0 to 2.5 GPa. The monoclinic phase is retained when the pressure is decreased. In (10,10) bundles, LDA results at 0.5 GPa showing large difference in values of *a* and *b* were obtained from two levels of optimizations as the convergence is very slow. This indicates that transition to monoclinic phase might occur even at lower pressure. For (12,12) bundles, there is a gradual decrease in the lattice parameter with increasing pressure. Lines are guides to the eye only.

strongly influence its interaction with adsorbate molecules due to changes in the σ-π bonding.

The oval-shaped nanotubes are packed more tightly than the cylindrical nanotubes and this contributes also to the increased van der Waals interactions between the flattened portions of nanotubes. For bundles of (12,12) nanotubes, however, the flattening occurs in the form of hexagonal deformation. Calculations up to 6 GPa show that the symmetry remains hexagonal [Fig. 1(d)]. The change in the lattice parameter with pressure is shown in Fig. 2(c). We also took an initial configuration of a monoclinic structure with oval (12,12) nanotubes. However, after structural optimization, it returned to a hexagonal structure with nanotube cross sections that are intermediate between circles and hexagons. The polygonization increases with pressure. The BE of 1.3 (11.2) meV/atom of (12,12) nanotubes in SWCNTB's is comparable to the value obtained for the (10,10) SWCNTB's. Thus, the absence of threefold symmetry of the nanotubes plays a crucial role in driving the monoclinic transformation in (10,10) SWCNTB's. The transition between the near-hexagonal and monoclinic structures can be interpreted as a competition between the energy gained by the increased intertube interaction provided by the flattening of the tube walls in the monoclinic structure, and the energy cost associated with the deformation from a circular to an oval shape. In the LDA, the intertubular interaction is much stronger while the deformation energy is about the same as in the GGA. Therefore, the balance between the two terms is reached at a lower pressure in the LDA than in the GGA.

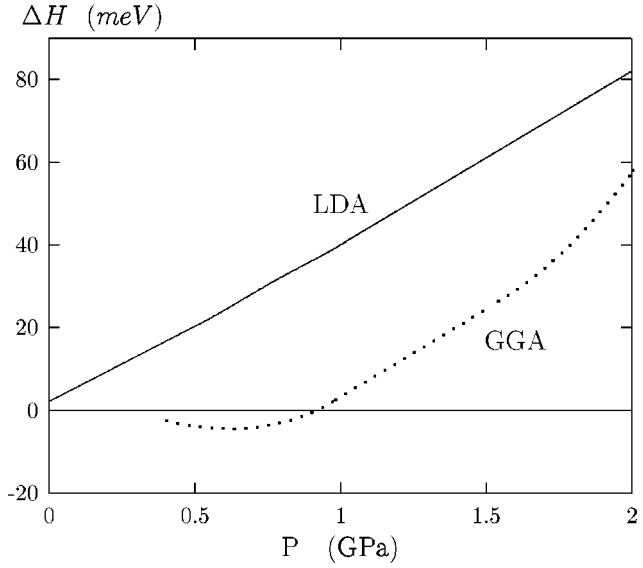

FIG. 3. Enthalpy of near-hexagonal phase minus the value for the monoclinic phase of (10,10) bundles as a function of pressure. In GGA the two phases are at equilibrium at a hydrostatic pressure of ≈ 1 GPa.

The electronic structure changes during the transformation.[17] Although (10,10) and (12,12) isolated nanotubes are electronically similarly metallic, when assembled in bundles they are clearly differentiated. In (12,12) SWCNTB's, quasi-band-gaps exist in all high-symmetry directions parallel to the Γ-*A* direction except for the *K*-*H* direction, where the valence and conduction bands just touch at a single point (0.6587 along *K*-*H*, slightly closer towards 2/3 than for the (6,6) tubes in Ref. 18). Under hydrostatic pressure this picture does not change. While the bands move

towards higher energies and the quasi-band-gaps increase most noticeably along the Γ-*A* direction, a single point where valence and conduction bands meet remains along the *K*-*H* direction (at a fraction of 0.6451 at 6 GPa). In (10,10) SWCNTB's, similar quasi-band-gaps exist along the high-symmetry directions parallel to the reciprocal of the tube axis. As the (10,10) SWCNTB has monoclinic rather than hexagonal symmetry, the hexagonal *K*-*H* direction has no high-symmetry equivalent and the *M*-*L* direction splits in three branches (*A*-*E*, *B*-*D*, and *Y*-*C*). Unlike the (12,12) case, the valence and conduction bands overlap at about $2\pi/3$ along the reciprocal of the tube axis, as was reported previously by Delaney *et al.*[19] The conduction band along the Γ-*Z* direction is well below the valence band along directions that would correspond to *K*-*H* and *M*-*L* directions in a hexagonal cell. Under hydrostatic pressure this feature remains unchanged.

In summary, we find that SWCNTB's with nanotubes, incommensurate with the threefold symmetry of the lattice, undergo a first-order phase transformation from a nearly hexagonal structure with cylindrical nanotubes to a monoclinic structure in which the nanotube cross section becomes oval, under hydrostatic pressure. The nonsymmetric nature of the intertube interaction is responsible for this transformation. As the ovalization results from a nanotube not being commensurate with the hexagonal arrangement of the tubes in a bundle, it follows that no matter how large a unit cell is chosen, the bonding with neighboring tubes will not be symmetric. Therefore, ovalization of an initially cylindrical tube will occur irrespective of the number of tubes in the unit cell. In (10,10) SWCNTB's the computed transition pressure is predicted to be in the range of 0 to 1 GPa, but it could be affected by the presence of nanotubes with other chiralities/diameters in a bundle. Our calculations also suggest that incommensurate nanotubes of about 14.0 Å diameter may actually have oval shape even at zero pressure. This is likely to be true even for smaller diameter tubes due to the very nature of interaction. SWCNTB's with nanotubes commensurate with the threefold symmetry of the lattice, do not undergo such a phase transition. Instead a gradual polygonization of the nanotubes occurs with increasing pressure. Therefore, the contradictory reports from experiments concerning the behavior of SWCNTB's under hydrostatic pressure is attributed to differences in the types of nanotubes present in bundles. SWCNTB's with nanotube diameters of ≈ 1.34 nm have no chiralities with threefold symmetry, so that a transformation to the monoclinic phase must occur under pressure as has been observed upon loading at pressures of 1.5 to 1.7 GPa. This finding is at variance with the results of Lopez *et al.*[8] in which only polygonization has been found and with those of Peters *et al.*[5] where the *tube diameter only* determines whether polygonization or ovalization occurs. The transformation is accompanied by a small volume effect only, but the unit-cell shape and the nanotube cross section change very considerably. These results suggest that such a transformation holds promise for applications such as microactuators and for pressure selective absorption.

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[1] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, and M.S. Dresselhaus, Science **286**, 1127 (1999).

[2] M. Winter, J.O. Besenhard, M.E. Spahr, and P. Novak, Adv. Mater. **10**, 7259 (1998).

[3] U.D. Venkateswaran, A.M. Rao, E. Richter, M. Menon, A. Rinzler, R.E. Smalley, and P.C. Eklund, Phys. Rev. B **59**, 10 928 (1999).

[4] J. Tang. L.-C. Qin, T. Sasaki, M. Yudasaki, A. Matsushita, and S. Iijima, Phys. Rev. Lett. **85**, 1887 (2000).

[5] M.J. Peters, L.E. McNeil, J.P. Lu, and D. Kahn, Phys. Rev. B **61**, 5939 (2000).

[6] S.A. Chesnokov, V.A. Nalimova, A.G. Rinzler, R.E. Smalley, and J.E. Fischer, Phys. Rev. Lett. **82**, 343 (1999).

[7] J. Tersoff and R.S. Ruoff, Phys. Rev. Lett. **73**, 676 (1994).

[8] M.J. Lopez, A. Rubio, J.A. Alonso, L.-C. Qin, and S. Iijima, Phys. Rev. Lett. **86**, 3056 (2001).

[9] U.D. Venkateswaran, E.A. Brandsen, U. Schlecht, A.M. Rao, E. Richter, I. Loa, K. Syassen, and P.C. Eklund, Phys. Status Solidi B **223**, 225 (2001).

[10] L. Henrard, A. Loiseau, C. Journet, and P. Bernier, Eur. Phys. J. B **13**, 661 (2000).

[11] It is possible that in (10,10) bundles, there are distortions in the structure that could lead to more than one nanotube per cell. However, in order to keep the calculations to a manageable level, only one nanotube per cell is considered.

[12] A. Thess *et al.*, Science **273**, 483 (1996).

[13] G. Kresse, J. Furthmüller, J. Comput. Mat. Sci. **6**, 15 (1996).

[14] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[15] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).

[16] Initial calculations were done in GGA with 7 **k** points, which showed structural transformation. Calculations between 0 and 2 GPa were repeated with 29 **k** points and these results are given in the figures. LDA calculations are done with 15 **k** points. The general conclusions are insensitive to the number of **k** points used.

[17] M.H. F. Sluiter, V. Kumar, Y. Kawazoe, Physica B (in press).

[18] J.C. Charlier, X. Gonze, and J.P. Michenaud, Europhys. Lett. **29**, 43 (1995).

[19] P. Delaney, H.J. Choi, J. Ihm, S.G. Louie, and M.L. Cohen, Nature (London) **391**, 466 (1998).